Mechanism of Defect Generation by Plasma Surface Interaction and Its Influence on Electronic Devices

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論文内容要旨

Improvement of information technology have based on the miniaturization of devices for the high-integration of metal-oxide-semiconductor field effect transistors (MOS-FETs). Since the beginning of the microelectronics era, the smallest line width or the minimum feature length of an integrated circuit has been reduced at a rate of about 13 % per year. At that rate, the minimum feature length will shrink about 50 nm in the year 2010. This miniaturization had been realized by the micro-fabrication processing, such as plasma etching and lithography. Lithography is the process of transferring patterns of circuits on a mask to radiation-sensitive material, which called photo-resist, covering the surface of the semiconductor wafer. Then, we could remove and fabricate the precise patterns by using plasma etching process. This plasma etching process could be the most promising method to fabricate the sub-100 nm structure of MOS devices. With controlling the plasma etching process precisely, it would be realize the more integrated and precise structures of MOS devices. Especially, to fabricate sub-50 nm devices, control of few nm scale fabrication is required. Namely, the atoms or molecule scale fabrication is required for the development of high-performance of sub-50 nm devices. In addition, photon radiation damages are the serious problem to realize the sub-50 nm devices. Especially, high energy ultraviolet (UV) photons generates the crystal defects on the surface and interface of devices. This crystal defects would be the fatal damage for controlling the electronic properties of the devices.

On the other hand, in order to breakthrough the limitation of the silicon MOS devices, molecular electronics is now investigating. The concept of the molecular electronics is the design of a molecular that itself is the active element. However, for the developing of molecular electronics, the UV radiation damages are more serious problems in organic molecules. Thus, the damage-free process is strongly require for the realization of molecular electronics.

In this thesis, damage-free plasma processes for fabrication of sub-50 nm LSI devices have been investigated in this thesis. To eliminate the radiation damages during plasma processes, the pulse-time-modulated (TM) plasma and neutral beam (NB) processes were investigated and the generation mechanism for UV radiation damages was understood.

In chapter 2 and 3, the UV radiation damages in silicon MOS devices were investigated. Additionally, the influences of UV irradiation from the plasma to organic molecules for advanced devices were investigated in chapter 4. In both cases, the damage-free processes were proposed for fabricating the advanced devices.

(1) UV radiation damages in silicon MOS devices (Chapter 2)

UV photon radiation damages during the plasma process were investigated. Generally, the UV photon generates the electron-hole pairs and it induces the degradation of MOS devices. There is, however, no further mechanism of the UV radiation damage during the plasma process. Therefore, we quantitatively measured 1) generation of electron-hole pairs; 2) generation of crystal defects; 3) degradation of MOS-FET devices to understand the relationship between the UV photon radiation and its induced damages.

The generation of electron-hole pairs measured using the on-wafer monitoring sensor. On-wafer monitoring sensor could measure the amount of electron-hole pairs as plasma-induced current in simple structure device during the plasma etching processes. Plasma-induced current depended on the UV photon energy (wavelength), photon flux, and also the penetration depth of UV photon. Therefore, the reduction of the UV photon radiation or the UV photon energy is much important to reduce the UV photon radiation damages. Furthermore, the amount of the plasma-induced current drastically changed by changing the structure of the dielectric films, because of the band gap energy of the films were different. From this point of view, we could propose not only the damage-free process but also the damage-free structure of devices for the UV radiation damages.

The Crystal defects generated by UV photon radiation were evaluated using the electron spin resonance (ESR) spectroscopy. After the plasma irradiation, E' center, which the silicon dangling bond in SiO_2 film, was measured. The amount of E' center generation depended on the UV photon energy and UV penetration depth to the SiO_2 film. This result indicates that the E' centers were generated by the UV radiation and it has the relationship between the generation of the electron-hole pairs.

Finally, we evaluated the UV radiation damages in actual MOS-FET devices, such as charge-coupled devices (CCDs). Dark current in CCD image sensor drastically increased after the plasma radiation. At the same time, the

SiO_2/Si interface state density, which measured by charge pumping method, increased. Additionally, generation both the dark current and interface state density strongly corresponded to the generation of UV photon intensity. Namely, the UV photon generates the interface state in SiO_2/Si interface, then the dark current in CCD image sensor increased.

Through these results, we understood that the UV photon radiation is one of the most important species for the degradation of silicon MOS devices. UV photon generates the electron-hole pairs in SiO_2 films. These generated electron-hole pairs creates the E' center in SiO_2 film and induce the interface state at SiO_2/Si interface. Especially, in CCD image senor, the interface states increase the dark current. Furthermore, for the fabrication of the sub-50 nm silicon devices, the creation of the crystal defects, such as E' centers, will be the serious problem for the degradation of device characteristics. Therefore, the reduction of UV radiation damages is strongly required for the future MOS devices.

(2) Reduction of UV radiation damages

Pulse-time-modulated (TM) plasma was investigated for the reduction of the plasma-induced UV photon radiation damages. During the TM plasma irradiation, the electron energy drastically decreased with maintaining the ion or radical density. As the electron energy decreases during plasma-off in the TM plasma, the UV photon irradiation drastically reduced and the UV radiation damage could be eliminated.

Plasma-induced current drastically reduced during the pulse-off period with reduction of UV photon radiation. This result indicated that the UV-induced electron-hole pair generation was reduce or electron and hole recombined during the pulse-off period.

The generation of E' center was also decreased using the TM plasma irradiation. This is because UV irradiation to the SiO_2 film was eliminated during the pulse-off period. Then, the electron energy of defects generated in the SiO_2 film by TM plasma irradiation was much lower than that in the case of CW plasma irradiation. Then, the recombination of electron and hole would be occurred in high probability, comparing with CW-plasma irradiation. Thus the stable defect, such as E' center could be reduced using the TM plasma irradiation.

Finally, we applied the TM plasma for the actual micro-lens fabrication of CCD image sensor. Using the TM plasma irradiation, the CCD dark current drastically eliminated especially in CF_4/O_2 plasma. The yield of CCD image sensor drastically improved from 65% to 100%.

Through these results, we understood that the TM plasma is effective for the reduction of UV radiation damages.

We investigated the reduction mechanism of UV radiation damages with using the on-wafer monitoring sensor, ESR, and positron annihilation measurement. And this mechanism could be applied to the reduction of the UV radiation damage in actual MOS devices. The TM plasma is promising candidate to fabricate the sub-50 nm LSI devices with the reduction of UV radiation damages.

(3) Damage-free surface modification of organic molecules

Molecular electronics are promising candidate for the fabrication of sub-10 nm electronic devices. In order to realize the molecular devices, the controlling the surface properties of molecular is quite important. The surface modification of molecules is strongly required. However these organic molecules were not so strong to the UV irradiation from plasma, comparing with silicon materials. Especially, UV photon broke the chemical bond of the molecules, and broke the molecular structures. In this chapter, I investigated the effect of plasma process, especially the UV photon radiation, for the modification of terphenyl methanethiol self-assembled monolayer (TP1-SAMs). This TP1-SAMs is expected for future organic molecular devices.

Using the plasma process, plasma-induced UV photons enhanced the surface etching reactions. As a result, the molecules were decomposed from the substrate of gold. This could not improve even using the pulse-time-modulated (TM) plasma, instead of reducing the UV photon radiation. Therefore, the damage-free surface nitridation process would be strongly required.

In order to eliminate the influence of UV irradiation, the neutral beam (NB) process was investigated. Using the NB process, no charged particles and no UV photons were transported to the molecular surface. As a result, NB process could realize the damage-free surface modification of the TP1-SAMs.

Additionally, the TM NB process could atomically control the amount of the surface nitridation of the TP1-SAMs.

From these results, we found that the UV-free process, neutral beam process could be the promising candidate to develop the future sub-10 nm organic molecular devices.

With miniaturizing silicon MOS devices, UV photon radiation damages will be more serious problems. Through this thesis, I clarified the effect of pulse-time-modulated (TM) plasma and the neutral beam (NB) processes for the reduction of the UV radiation damages in the organic and inorganic materials. As a result, these processes will be strong promising candidate to breakthrough the limitation of device miniaturization.

論文審査結果の要旨

半導体デバイスの高集積化と高機能化を実現するために、配線パターン寸法の微細化が行われてきた。この微細化の発展は、半導体製造プロセス技術の進歩によって支えられてきた。特に、反応性プラズマを用いたエッチング技術の著しい向上により微細化が促進されてきたといっても過言ではない。しかしながら、50nmを切る超微細なデバイス製造プロセスにおいては、従来にもまして高精度な加工技術が必要不可欠となり、エッチング特性を左右するプラズマ中の生成活性種とそのエネルギーの制御およびプラズマ照射損傷を引き起こす基板表面への蓄積電荷量やフォトン照射量の制御が大きな課題になっている。本論文では以上の問題を解決するために、特にプラズマから照射される紫外線の影響を詳細に調べ、紫外線による欠陥生成メカニズムを考察するとともに、半導体素子への影響を示している。さらに、この欠陥生成を抑制する手法としてパルス変調プラズマおよび中性粒子ビームを検討し、その有効性を実証したもので、全編５章よりなる。

第１章は序論であり、本研究の背景や目的を述べている。

第２章では、半導体製造プロセスにおけるプラズマエッチング中の紫外線照射損傷について議論している。反応性プラズマから発生する紫外光スペクトル、プラズマ照射中に絶縁膜中に誘起する電流、絶縁膜中に生成される欠陥密度およびＭＯＳトランジスタにおける界面準位と固体撮像素子における暗電流との関係について詳細に検討している。膜材料のバンドギャップ以上のエネルギーを持った紫外線が照射されると電子励起が起こり、正孔・電子対が形成され絶縁膜中に誘起される電流（プラズマ誘起電流）として検出されることが分かった。このプラズマ誘起電流は、膜中や界面に形成される欠陥密度や界面準位と対応し、プラズマ誘起電流の測定により実際のデバイス構造における紫外光照射損傷を予測できることを示している。また、この手法を用いることで、プラズマエッチングプロセスにおける紫外線の放射はデバイス特性を大幅に劣化させることを定量的に明らかにしている。これらは実用上極めて有益な成果である。

第３章では、プロセス特性を維持しながらプラズマからの紫外線照射を抑制できるパルス変調プラズマの効果について議論している。数十μ秒で高周波電界を ON/OFF するパルス変調プラズマでは、活性種の生成時定数と消滅時定数の違いから、従来の連続放電プラズマと同等の活性種密度を維持した状態で、OFF 時間中では電子エネルギーが低くなり紫外線の放射が抑制されることを示している。このとき、表面にできる欠陥は従来のプラズマエッチングプロセスに比べて大幅に抑制されることを明らかにしている。これは、紫外線照射による膜中欠陥生成時定数が数十μ秒であることによると考えられ、パルス変調プラズマによるエッチングを適用したデバイスにおける電気特性も大幅に向上することを示している。これらは実用上極めて有益な成果である。

第４章では、ポストシリコンデバイスとして注目されている有機分子素子におけるプラズマ処理中の紫外線照射損傷について議論している。有機分子はシリコンやシリコン酸化膜のような無機材料に比べて紫外線照射耐性が低く、通常の連続放電プラズマやパルス変調プラズマでは簡単に分子構造が破壊されることを示している。そこで、紫外線を充分抑制できる中性粒子ビームプロセスを適用し、有機分子構造を維持したまま表面を改質（窒化）することができることを明らかにしている。将来デバイスでは、トップダウン方式とボトムアップ方式の融合、無機材料と有機材料の融合などが必要不可欠であり、中性粒子ビームプロセスにより実現できることを示唆している。こられは実用上極めて有益な成果である。

第５章は結論である。

以上、要するに本論文は、反応性プラズマにおける物理・化学現象を明らかにし、実際の半導体デバイス製造プロセスにおいて問題となる紫外線照射損傷の生成メカニズムを考察するとともに、それらを解決する手段としてパルス変調プラズマプロセスや中性粒子ビームプロセスという従来にはない手法を検討し、その有効性を実際の半導体デバイス上で示したもので、その成果は、50nm 以下の次世代半導体デバイス製造に適用可能であり、機械知能工学の発展に寄与するところが少なくない。

よって，本論文は博士（工学）の学位論文として合格と認める。